



S/N 10/809033

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	SASAKI ET AL.	Examiner:	G. Nagesh RAO
Serial No.:	10/809033	Group Art Unit:	1722
Filed:	MARCH 25, 2004	Docket No.:	10873.1440US01
Title:	METHOD OF MANUFACTURING GROUP III NITRIDE SINGLE CRYSTAL, DEVICE USED FOR THE METHOD AND GROUP III NITRIDE SINGLE CRYSTAL OBTAINED BY THE METHOD		

CERTIFICATE UNDER 37 CFR 1.6(d):

I hereby certify that this paper is being transmitted by email to the U.S. Patent and Trademark Office on April \_\_, 2007.

By: \_\_\_\_\_

Name: Tracy Kimmel

Mail Stop: AMENDMENT  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

DECLARATION UNDER 37 C.F.R. §1.132

Dear Sir:

I, Mamoru Imade, a citizen of and residing in Japan, hereby declare as follows:

I am an inventor in the instant U.S. patent application 10/809033.

I have conducted the following experiments and obtained the resulting experimental data.

## **Experimental results**

### **1. Object of the Experiments**

These experiments were conducted to show that the present invention is directed to a method for manufacturing a GaN single crystal by using an aeriform substance that includes GaH<sub>x</sub>.

### **2. Description of the Experiment**

#### **(1) Experiment 1**

Conditions:

Material: metal Ga

Atmospheric gas: N<sub>2</sub> (100%)

Carrier gas: N<sub>2</sub> (90%) + H<sub>2</sub> (10%) mixed gas, flow rate of 200 sccm

Pressure: 1 atm (0.1 MPa)

Temperature: 950, 975, 1000, 1025, 1050, 1075, 1100°C

Time: 1 hour

Method:

5 g of metal Ga was put in a crucible, and the crucible was placed in a pressure-resistant chamber. A carrier gas containing H<sub>2</sub> was sprayed on the surface of the metal Ga, and then Ga was evaporated at each temperature for a predetermined time. The evaporation rate (g/h) of Ga was calculated from the decrement of the metal Ga.

#### **(2) Experiment 2**

Conditions:

Apparatus: The apparatus as shown in FIG. 2A of the present application

Material: GaN powder

Atmospheric gas: N<sub>2</sub> (100%)

Carrier gas: N<sub>2</sub> (90%) + H<sub>2</sub> (10%) mixed gas, flow rate of 200 sccm

Pressure: 5 atm (0.5 MPa)

Temperature: 1080, 1090, 1100, 1120, 1130, 1150, 1190°C

Time: 30 minutes

**Method:**

4 g of GaN powder was put in a crucible, and the crucible was placed in a pressure-resistance chamber. A carrier gas containing  $H_2$  was supplied, and then GaN powder was evaporated at each temperature for a predetermined time. The evaporation rate (g/h) was calculated from the decrement of the GaN powder.

**3. Results of the Experiments**

**(1) Experiment 1**

(a) FIG. 1 shows a graph A that plots the evaporation rate of the metal Ga (vertical axis) versus temperature ( $10000/T(K^{-1})$ ) (horizontal axis).

The evaporation energy ( $\Delta E$ ) of the metal Ga was determined by the slope of the graph A that indicates the temperature dependence of the evaporation rate.

The evaporation energy thus obtained was 1.6 eV, which agreed with the theoretical value (1.6 eV) relating to the evaporation of  $GaH_2$ . This makes it clear that the metal Ga is evaporated to form  $GaH_2$ .

Consequently, the aeriform substance produced by heating the metal Ga in the presence of  $H_2$  can be  $GaH_2$ .

(b) An aeriform substance ( $GaH_2$ ) produced under the same conditions as those in the method (a) and a reactant gas (100% ammonium gas, flow rate of 200 sccm) reacted in the crystal growth region, so that a GaN crystal with a thickness of 10  $\mu m$  was formed (FIG. 2).

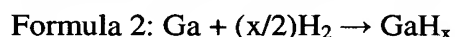
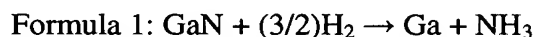
**(2) Experiment 2**

(a) FIG. 1 shows a graph B that plots the evaporation rate of the GaN powder (vertical axis) versus temperature ( $10000/T(K^{-1})$ ) (horizontal axis).

The evaporation energy ( $\Delta E$ ) of the GaN powder was determined by the slope of the graph B that indicates the temperature dependence of the evaporation rate.

The graph B has an inflection point at 1100°C (1373 K). The evaporation energy was 1.68 eV at 1100°C or more and 6.57 eV at 1100°C or less. The inflection point is attributed to the use of the GaN powder as a material, since the evaporation of  $GaH_x$  may

involve two steps of reactions, i.e., the decomposition of GaN and the generation of GaH<sub>x</sub>, as expressed by the following formulas, respectively.



When the temperature is 1100°C or more, the GaN decomposition reaction (Formula 1) is sufficiently faster than the GaH<sub>x</sub> generation reaction (Formula 2). Therefore, the GaH<sub>x</sub> generation reaction (Formula 2) may be in a rate-determining step in the process of evaporation of GaN. When the temperature is 1100°C or less, the GaN decomposition reaction (Formula 1) is sufficiently slower than the GaH<sub>x</sub> generation reaction (Formula 2). Therefore, the GaN decomposition reaction (Formula 1) may be in a rate-determining step in the process of evaporation of GaN (= GaH<sub>2</sub>).

Consequently, the aeriform substance produced by heating GaN powder in the presence of H<sub>2</sub> can be GaH<sub>2</sub>.

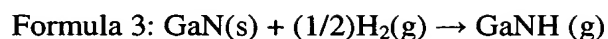
(b) An aeriform substance (GaH<sub>2</sub>) produced under the same conditions as those in the method (a) and a reactant gas (100% ammonium gas, flow rate of 200 sccm) reacted in the crystal growth region, so that a GaN crystal with a thickness of 60 μm was formed (FIG. 3).

#### 4. Brief discussion that GaNH is not present.

FIG. 4 shows a XRD profile of the GaN powder used in Experiment 2.

As can be seen from FIG. 4, all the detected peaks indicate GaN, and there are no GaNH species in the starting material.

Assuming that the GaN powder reacted with a hydrogen gas to produce GaNH after the experiment started (see Formula 3) and the GaNH evaporated, the activation energy (ΔE = 1.68 eV) derived from FIG. 1 should be different from the evaporation energy (ΔE = 1.60 eV) of GaH<sub>x</sub>. Moreover, no evidence shows that the evaporation energy of GaNH is present. Therefore, it is appropriate that the aeriform substance is considered as GaH<sub>x</sub>.



## 5. Conclusion

The above results confirmed that the aeriform substance including  $\text{GaH}_x$  was present in the reaction systems of Experiments 1 and 2, and as required by claim 1 of this patent application. Thus, the present invention is directed to a method for manufacturing a GaN single crystal by using the aeriform substance that includes  $\text{GaH}_x$ .

As shown by the experimental results, the aeriform substance produced is  $\text{GaH}_2$ , such as while using the nitrogen containing GaN powder and using mixed carrier gases as  $\text{N}_2$ , which are recited in some of the dependent claims of this patent application. I further declare that similar results can be obtained using the other nitrogen containing materials and nitrogen containing carrier gases, such as those listed in the dependent claims of the instant patent application, and which are not specifically tested in this Declaration.

FIG.1

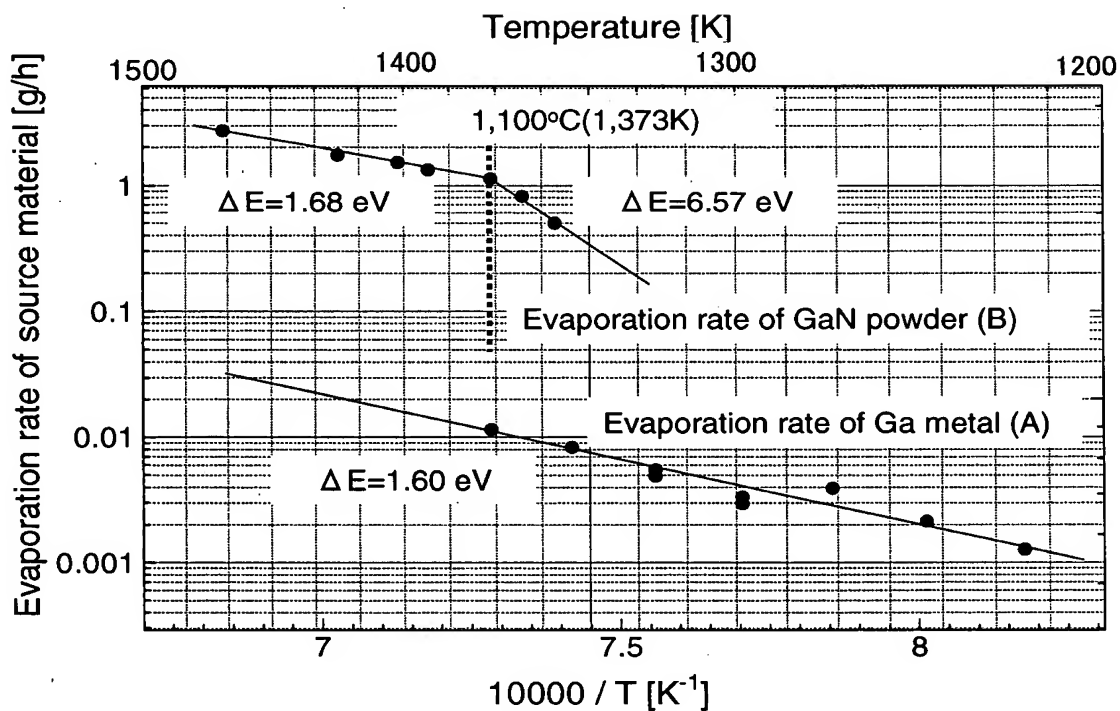


FIG.2

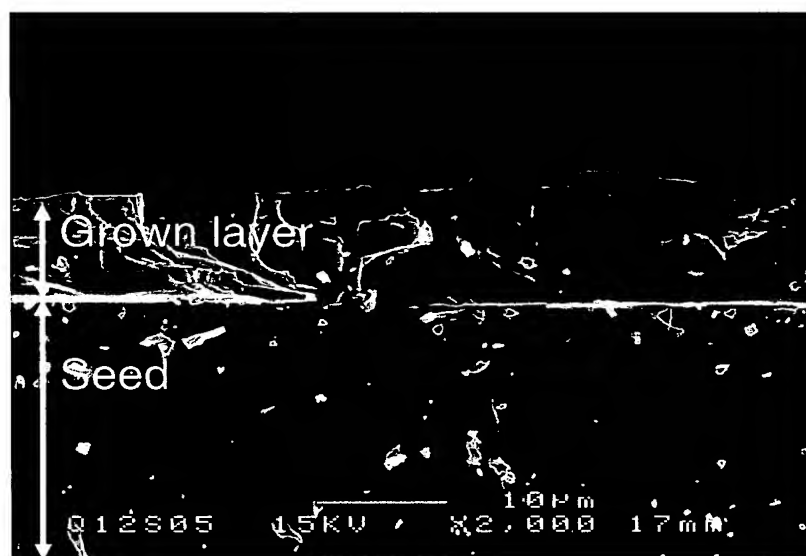


FIG.3

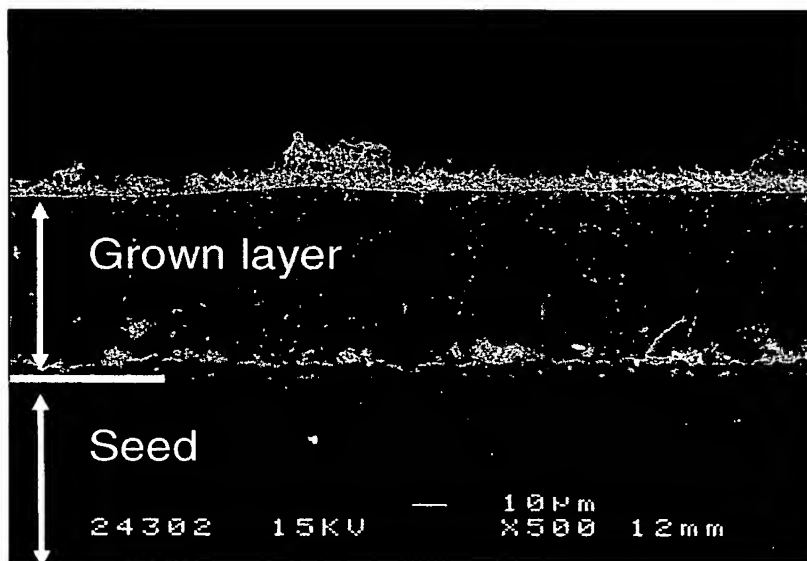
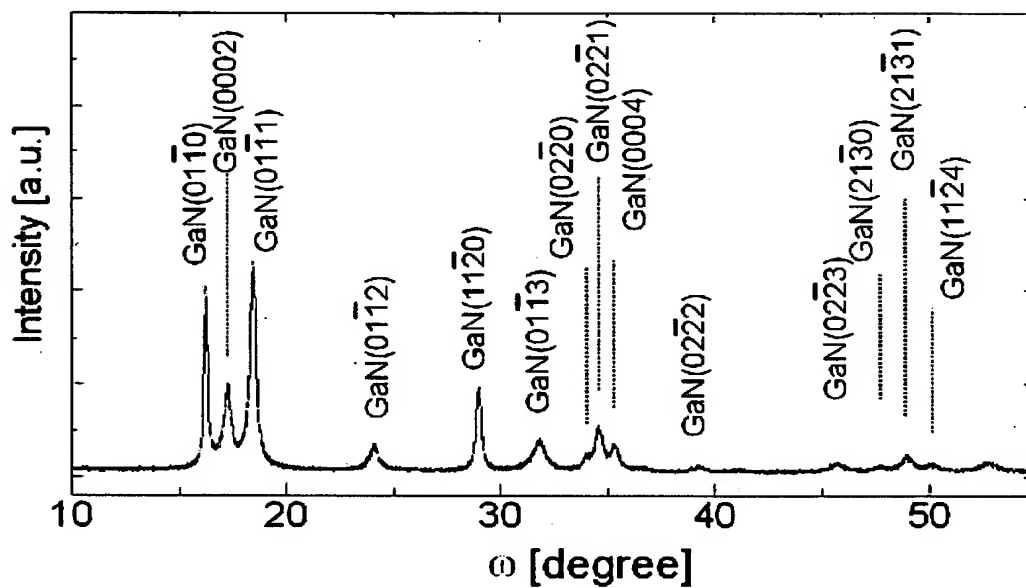


FIG.4



I declare under the penalty of perjury of the laws of the United States that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, with the knowledge that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: April 3, 2007

Signature: Mamoru Imade  
Mamoru Imade